



## New diagnostic ratios based on phenanthrenes and anthracenes for effective distinguishing heavy fuel oils from crude oils



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### ABSTRACT

The heavy fuel oils (HFOs) and crude oils are the main oil types in the marine oil spill accidents in China. It is usually a challenge to distinguish the HFOs from crude oils due to the highly similar physicochemical characteristics. In this paper, the distributions of phenanthrene (Phe), anthracene (Ant), methyl-phenanthrene (MP) and methyl-anthracene (MA) in hundreds of HFOs and crude oils samples which were collected from all over the world were characterized. Nine new diagnostic indexes, such as Ant/(Ant + Phe) and other eight diagnostic ratios based on the MP isomers and MA, were developed for effective distinguishing HFOs from crude oils. The histogram with normal fit plots, the double ratio plots and Bayes discriminant analysis (BDA) method were employed to illustrate the effectiveness of the new diagnostic indexes. BDA model based on nine new diagnostic indexes demonstrated high precision with discriminant ratio which lay between 93.92% and 99.32%.

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### 1. Introduction

China is the second largest oil consumer and the fifth largest oil producer in the world (Li et al., 2009). Owing to increasing transportation of petroleum by ocean going tankers and extensive exploitation of marine petroleum, marine and coastal environments are particularly vulnerable to petroleum pollutants in China. According to correlative statistic data, there were a total of 2635 oil spill accidents in offshore China from 1973 to 2006. The spilled oil mainly consists of the heavy fuel oils (HFOs) from ships and crude oils from oil platforms in China at present. After the oil spill accidents, successful forensic investigation and identification of oil type timely and accurately is extremely important for settling disputes related to liability selecting of spill response and taking effective clean-up measures (Wang and Fingas, 2003). Currently, the common approach to the characterization of spilled oil samples and identification of the potential source relies on analyses by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). Correlations are developed on the basis of the molecular distribution of aliphatic and aromatic hydrocarbons, or more specifically steranes and terpanes biomarker fingerprints (Wang and Fingas,

2003), however, the identification of HFOs and crude oils is extremely difficult.

HFOs, which are abundant with non-hydrocarbon compounds, resin and asphaltene, and are mainly derived from the residues of various refinery distillation and cracking processes, share the similar physical properties and chromatographic characteristics with crude oils. There is high risk that draws erroneous conclusions sometimes without knowledge of the type of spilled oil. It is urgent to establish the fingerprint identification method of HFOs and crude oils with more and more demands on oil source identification in spilled oil accidents.

Crude oils and the refined products with different sources often show different polycyclic aromatic hydrocarbon (PAH) distributions. Many PAH compounds are more resistant to weathering than their saturated hydrocarbon counterparts, which make PAHs as one of the most valuable fingerprinting classes of hydrocarbons for oil identification. A series of target alkylated PAH species have been successfully used as indicators for oil spill identification (Yunker et al., 2002; Wang and Fingas, 2003; Zhou et al., 2014). Ratios of individual source-specific isomers within the same alkylation level and the relative distributions of isomer-to-isomer have been used for oil spill source identification (Fayad and Overton, 1995; Wang and Fingas, 2003; Yim et al., 2011).

In this work, the distributions of phenanthrene (Phe), anthracene (Ant), methyl-phenanthrene (MP) and methyl-anthracene (MA) in hundreds of HFOs and crude oils samples were analyzed in detail.

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Furthermore, a number of new diagnostic indexes based on Phe, Ant, MP and MA were developed for effective distinguishing HFOs from crude oils.

## 2. Materials and methods

210 HFOs and 230 crude oils samples were mainly collected from China, Kingdom of Saudi Arabia, Iraq, Kuwait, Venezuela, Korea, Singapore, etc. Approximately 0.15 g pure oil samples were extracted with 10.0 mL of high purity *n*-hexane (Merck, HPLC, German)/dichloromethane (Merck, HPLC, German) (1:1, v/v), and about 1.00 g of anhydrous sodium sulfate was added to remove water. The mixture was vortexed for 30 s, and then centrifuged at 3000 r.p.m. for 5 min. After that, 1.0 mL of the supernatant was transferred to a vial containing 1.00 g of silica gel. 5.0 mL of high purity *n*-hexane/dichloromethane (1:1, v/v) was added to the vial. The mixture was vortexed and then centrifuged at 3000 r.p.m. An aliquot of 1.0 mL of each extract was subjected to analysis.

The treated oil samples were analyzed with 7890A GC-5975C MS (Agilent Technologies, USA) equipped with a HP-5MS fused silica capillary column (60 m, 0.25 mm i.d., 0.25  $\mu$ m film thickness, J&W Scientific, USA) in the pulsed splitless mode. The GC oven temperature was programmed from 60 to 300 °C at 6 °C/min, and maintained at 300 °C for 30 min. Helium was used as carrier gas with 1.0 mL/min constant flow. The temperature of injector, transfer line and ion source were 290 °C, 280 °C and 230 °C, respectively.

Qualitative analysis of oil samples was performed in selected ion monitoring (SIM) mode. All samples were analyzed twice in order to eliminate the effect of analytical variability and sample heterogeneity.

## 3. Results and discussion

Molecular indices based on the ratios of individual PAH levels can be used to assess the origin of PAHs (Yunker et al., 2002; Marusenko et al., 2011). For example, phenanthrenes are dominant aromatic hydrocarbons in most of the oils and mass 178 is commonly used to distinguish between combustion and petroleum sources (Yunker et al., 2002). The oil samples often contain five methyl-phenanthrenes (MPs) (in two pairs of doublet peaks: 3- and 2-, 9-/4- and 1-MP). In general, 3- and 2-MP ( $\beta$ -type) isomers are more stable than the 9-/4- and 1-MP ( $\alpha$ -type) isomers (Rdake et al., 1986; Wang and Stout, 2007).

### 3.1. Distribution of Phe, Ant, MP and MA

The peak identifications were summarized in Fig. 1 combining representative chromatograms for the Phe, Ant, MP and MA of HFO and crude oil. The relative abundance of Ant in crude oil was less than that of HFO. In addition, the relative abundance of 2-methyl-anthracene (2-MA) in crude oil was also lower than that of HFO. MA, particular 2-MA, was suggested to be produced under some pyrolytic conditions experienced in the course of refining (e.g., thermal cracking). Based on this, the presence of 2-MA might be served as an effective indicator to distinguish HFOs from crude oils.

### 3.2. Ant to Ant plus Phe ratio

For mass 178, the values of Ant to Ant plus Phe ratio ( $\text{Ant}/(\text{Ant} + \text{Phe}) < 0.10$ ) are characteristic of petroleum input or diagenetic sources, whereas values  $> 0.10$  are the feature of combustion processes (Budzinski et al., 1997; Yunker et al., 2002).

The histogram with normal fit plots of  $\text{Ant}/(\text{Ant} + \text{Phe})$  values of HFOs (Fig. 2a) and crude oils (Fig. 2b) were drawn by histfit function of MATLAB software (R2014a). The ratio of  $\text{Ant}/(\text{Ant} + \text{Phe})$  ranged from 0.05 to 0.37 for HFOs. In contrast, the  $\text{Ant}/(\text{Ant} + \text{Phe})$  values of crude oils were mainly concentrated in the vicinity of 0.02, and only a

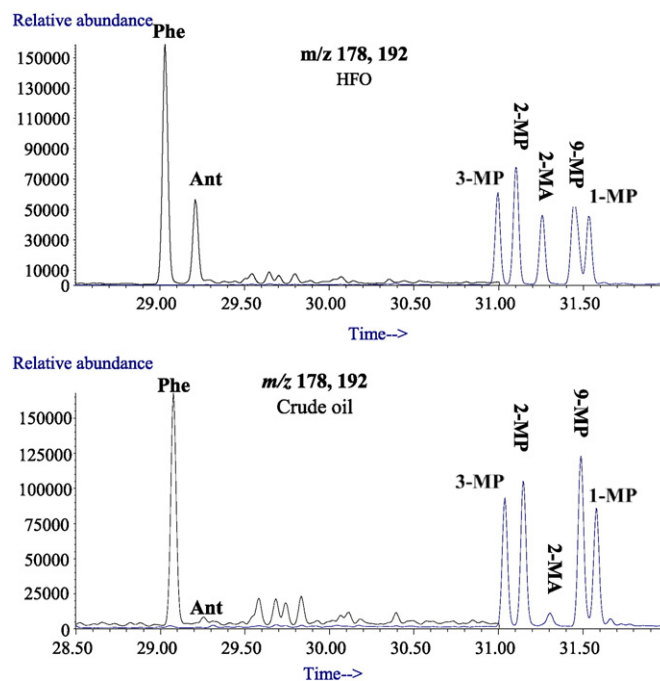


Fig. 1. Mass-chromatograms of mass 178, 192 (Phe, Ant, MP and MA) of HFO and crude oil.

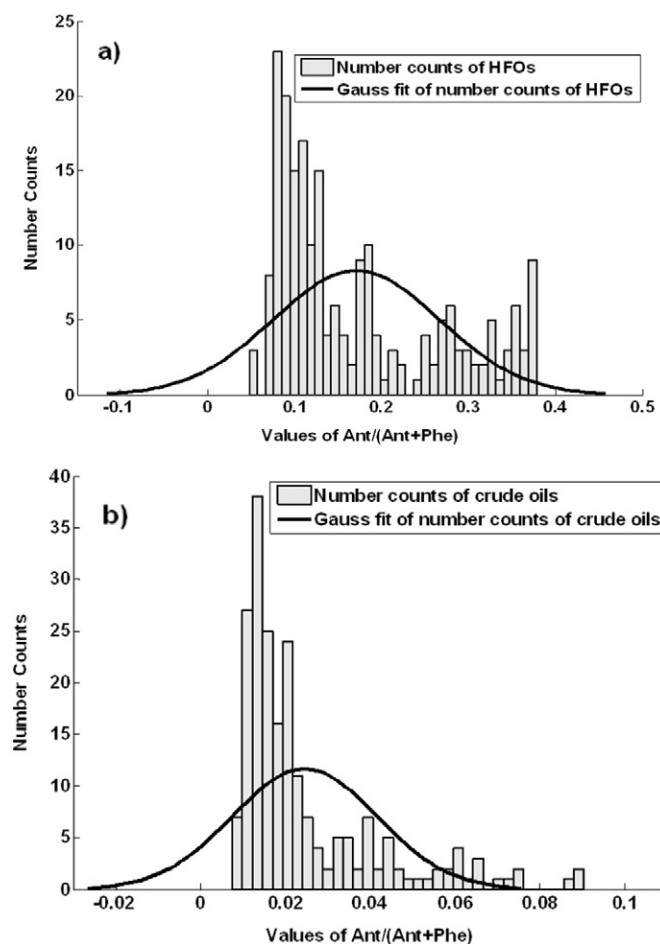


Fig. 2. Histogram with normal fit plots of  $\text{Ant}/(\text{Ant} + \text{Phe})$  values of HFOs (a) and crude oils (b).

small portion of the ratio exceeded 0.05. In summary, Ant/(Ant + Phe) values of crude oils samples were lower than those of HFOs.

### 3.3. Double ratio plots of MP isomers and MA

The proportions of the five MP isomers (which appear as four prominent peaks in the  $m/z$  192 mass chromatogram of most oils) have been

widely used to monitor the thermal stress under geological heating of coals and oils (Yawanarajah and Kruger, 1994; Sivan et al., 2008).

In this work, a suite of diagnostic ratios based on MP isomers and MA were proposed to differentiate HFOs and crude oils. Double ratio plots of 2-MA/2-MP vs. 2-MA/3-MP ratios (Fig. 3a), 2-MA/1-MP vs. 2-MA/9-MP ratios (Fig. 3c), 2-MA/(3- + 2-) MP vs. 2-MA/(9- + 1-) MP ratios (Fig. 3e) and (3- + 2-) MP/(9- + 1-) MP vs. 2-MA/ $\Sigma$ MP ratios (Fig. 3g) were shown in Fig. 3. For clarity, the overlap region of HFOs

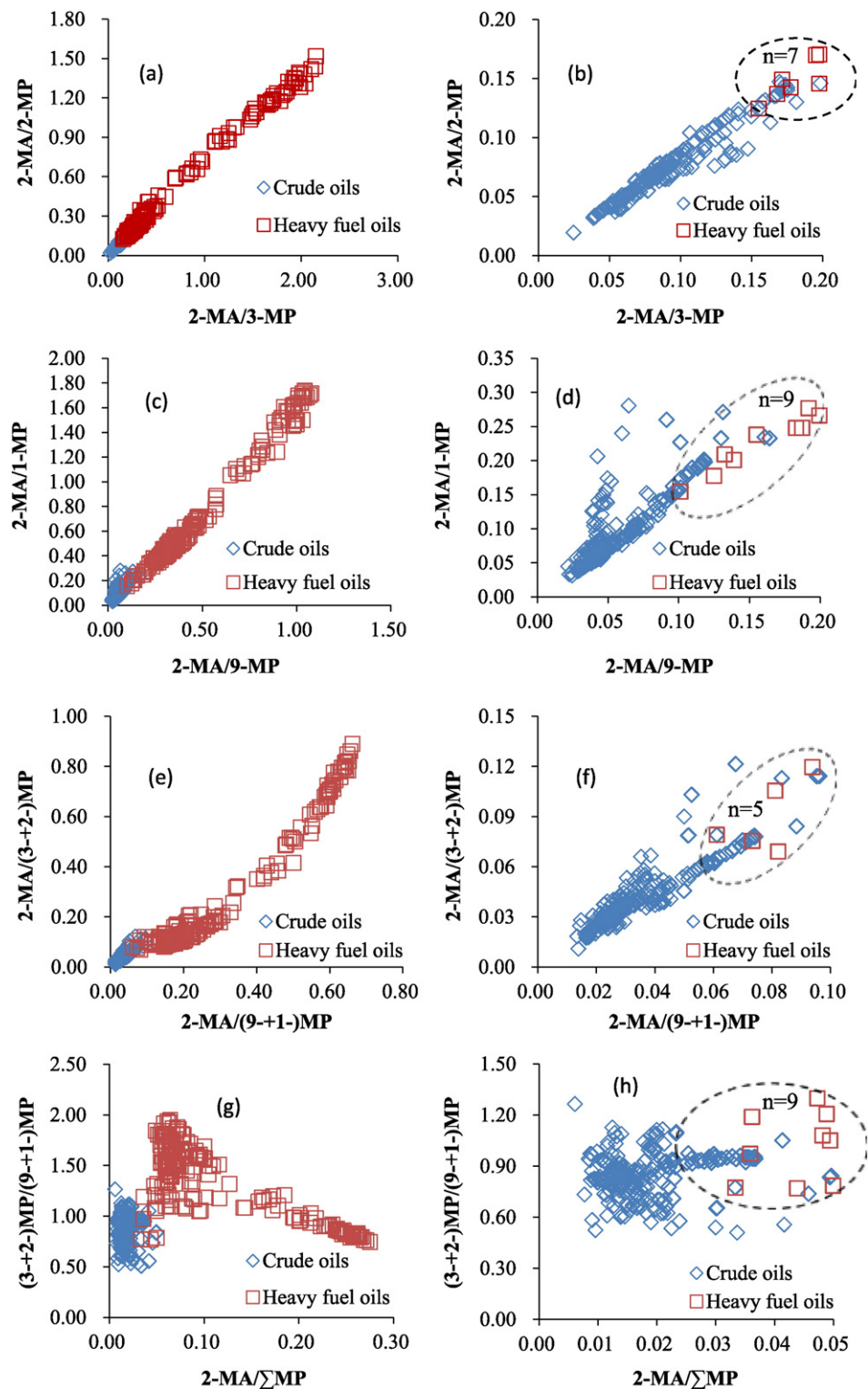


Fig. 3. Double ratio plots of 2-MA/2-MP vs. 2-MA/3-MP ratios (a), 2-MA/1-MP vs. 2-MA/9-MP ratios (c), 2-MA/(3- + 2-) MP vs. 2-MA/(9- + 1-) MP ratios (e), (3- + 2-) MP/(9- + 1-) MP vs. 2-MA/ $\Sigma$ MP ratios (g) and the corresponding enlarged drawings of overlap region of HFOs and crude oils for each pair of ratios (b, d, f, h).

and crude oils for each pair of ratios were enlarged (Fig. 3b, d, f, h). It was shown that HFOs and crude oils were well distinguished according to enlarged drawings. 2-MA/2-MP and 2-MA/3-MP ratios < 0.20 were associated with crude oils. Except for 7 HFO samples, 2-MA/2-MP and 2-MA/3-MP ratios of the majority of HFOs (more than 96.68%) were > 0.20 (Fig. 3b). In addition, 2-MA/1-MP ratio < 0.30 and 2-MA/9-MP ratio < 0.20 belonged to crude oils. With the exception of 9 HFO samples, 2-MA/1-MP and 2-MA/9-MP ratios of the majority of HFOs (more than 95.73%) were higher than 0.30 and 0.20, respectively (Fig. 3d). For crude oils, 2-MA/(3- + 2-) MP ratio and 2-MA/(9- + 1-) MP ratio were below 0.10 and 0.15, respectively. Except 5 HFO samples, 2-MA/(3- + 2-) MP and 2-MA/(9- + 1-) MP ratios of the majority of HFOs (more than 97.63%) were above 0.10 and 0.15, respectively (Fig. 3f). For crude oils, (3- + 2-) MP/(9- + 1-) MP ratio was below 0.05 and 2-MA/ $\Sigma$  MP ratio was below 1.50. Apart from 5 HFO samples, the values of (3- + 2-) MP/(9- + 1-) MP ratio and 2-MA/ $\Sigma$  MP ratio of the majority of HFOs (more than 97.63%) were above 0.05 and 1.50, respectively (Fig. 3h). In summary, above mentioned ratios of crude oils samples were lower than those of HFOs.

It is reasonable that the linear MA is considerably less thermodynamically stable than the nonlinear MP. Therefore, MA is absent or presents lower concentrations relative to MP in most crude oils under geologic heating conditions. As for HFOs, the relative abundance of MA will be increased due to the course of refining.

#### 3.4. Distinguishing results based on Bayes discriminant analysis

Bayes discriminant analysis (BDA) is a kind of commonly used classification method, which distinguishes new samples and classifies them into known groups (Xu et al., 2013). In this section, BDA method running on MATLAB software (R2014a) was applied to demonstrate the effectiveness of new diagnostic indexes to distinguish HFOs and crude oils. Nine diagnostic indexes (Ant/(Ant + Phe), 2-MA/2-MP, 2-MA/3-MP, 2-MA/1-MP, 2-MA/9-MP, 2-MA/(3- + 2-) MP, 2-MA/(9- + 1-) MP, (3- + 2-) MP/(9- + 1-) MP and 2-MA/ $\Sigma$  MP ratios) and their combinations were selected as discriminant indexes. 153 HFOs and 140 crude oils samples were chosen as training samples to establish discriminant analysis model, and 77 HFOs and 70 crude oils were used as test samples. The discriminant results were shown in Table 1. The results showed that BDA model had high precision and discriminant ratio lay between 93.92% and 99.32%. As for the highest recognition rate, the combinations of diagnostic indexes were 2-MA/9-MP vs. 2-MA/1-MP, 2-MA/9-MP vs. 2-MA/(9- + 1-) MP and 2-MA/1-MP vs. 2-MA/(9- + 1-) MP.

## 4. Conclusion

It is urgent and crucial to establish a method for effective distinguishing HFOs from crude oils. Nine new diagnostic indexes, based on Phe, Ant, MP and MA had been developed for discriminating between HFOs and crude oils. The histogram with normal fit plots based on Ant/(Ant + Phe) ratio illustrated that Ant/(Ant + Phe) values

of crude oils samples were lower than those of HFOs. According to the double ratio plots of 2-MA/2-MP vs. 2-MA/3-MP ratios, 2-MA/1-MP vs. 2-MA/9-MP ratios, 2-MA/(3- + 2-) MP vs. 2-MA/(9- + 1-) MP ratios and (3- + 2-) MP/(9- + 1-) MP vs. 2-MA/ $\Sigma$  MP ratios, the HFOs and crude oils samples were well distinguished. Moreover, BDA model based on nine new diagnostic indexes also demonstrated high precision and the discriminant ratio lay between 93.92% and 99.32%. These results could have great potential for application in tracing the source of spilled oil in complex situations.

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**Table 1**  
Discriminant results based on Bayes discriminant analysis.

Number of parameters used to combine	Highest recognition rate	Lowest recognition rate
1	98.65%	93.24%
2	99.32%	93.92%
3	98.65%	93.92%
4	98.65%	96.62%
5	98.65%	97.97%
6	98.65%	97.97%
7	98.65%	97.97%
8	98.65%	97.97%
9	98.65%	98.65%